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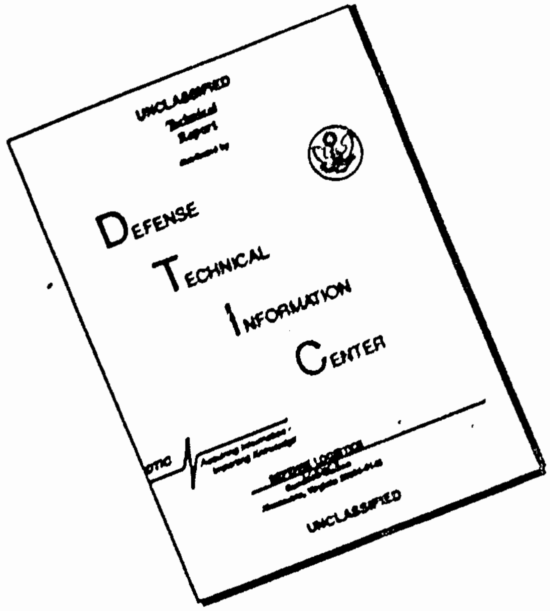

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United States Atomic Energy Commission

Division of Technical Information

OTI-131(May 1962)

$2.60

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee

RESEARCH ON

TANTALUM AND MOLYBDENUM BRAZING TECHNIQUES

QUARTERLY PROGRESS REPORT NOR 63-178

OCTOBER 1963

DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

PROJECT NO. 7351, TASK NO. 735102

(Prepared under Contract No. AF33(657)-11227
by Northrop Norair, A Division of Northrop
Corporation, Hawthorne, California
A. H. Freedman and E. B. Mikus, Authors)

FOREWORD

This report was prepared by Northrop Norair, A Division of Northrop Corporation, under USAF Contract No. AF33(657)-11227. The research activities related herein represent the 1st quarter effort covering the period of July through September 1963.

The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. R. E. Bowman serving as project engineer.

The program at Northrop Norair was performed under the direction of Dr. E. B. Mikus, Head of the Metallics Research Branch with Mr. A. H. Freedman serving as principle investigator and Mr. D. M. Brandt serving as project administrator.

Included among those who made major contributions in the research and/or the preparation of this technical report were: Messrs. L. H. Stone, R. R. Wells, H. E. Langman, J. W. Lewis, and H. R. Miller.

Publication Review
Approved by:

R. L. Jones

Dr. R. L. Jones
Chief, Materials Research Group

ABSTRACT

Brazed molybdenum and tantalum alloy honeycomb structures offer good potential for structural and heat shield applications in the 2500 - 3500F range. However, molybdenum is seriously embrittled at braze temperatures above approximately 2500F. Tantalum alloys are not embrittled by high braze temperatures, but there are serious production problems associated with braze temperatures above 3000F. The purpose of this program is to develop molybdenum and tantalum braze systems which braze at relatively low temperatures, but develop high remelt temperatures. Some attention is also being directed to the development of braze alloys for tantalum that braze several hundred degrees above the expected service temperature. Most of the effort will be based on the TZM molybdenum alloy and the Ta-10W alloy. Some work will be performed using the Ta-8W-2Hf and Ta-30Cb-7.5V alloys.

A literature survey was conducted which indicated that: (1) No completely satisfactory conventional or high remelt temperature braze systems have been developed for molybdenum and tantalum, (2) The diffusion sink and reactive brazing concepts offer the most potential for increasing joint remelt temperatures, (3) titanium-base alloys offer the most promise for molybdenum and tantalum diffusion sink braze alloys, and (4) columbium-base alloys offer the most promise for conventional brazing of tantalum.

A number of diffusion sink braze alloys have been developed and will be evaluated on tee joints. The molybdenum braze alloys are: Zr-25 Ti-32V, Ti-8Ni-7Si, Ti-25Cr-10Ni, and Zr-34Ti-33V. The tantalum braze alloys are: Zr-25Ti-32V, Ti-27V-7Fe, Ti-29V-2Si, Ti-28Zr-16Mo-10Ta, and Ti-21.5V-1.5Si-25Ta. These braze alloys will utilize diffusion sink additions of molybdenum and/or tantalum. Reactive brazing will incorporate additions of carbon and/or boron. The Cb-25V and Cb-30Ti alloys have been selected for conventional brazing of tantalum.

Pre-braze cleaning procedures for tantalum and molybdenum have been selected and their applicability verified experimentally.

Methods have been developed for placing diffusion sink powders at fillet and node areas on honeycomb specimens. These methods are capable of good control as well as applicability to a manufacturing operation.

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I INTRODUCTION

The general goal of this program is to develop braze alloys and techniques for the fabrication of molybdenum and tantalum alloy honeycomb panels for heat shield and other re-entry vehicle structures. The program is primarily based upon the concept of brazing and coating at relatively low temperatures with systems that develop substantial increases in joint remelt temperatures so as to permit high service temperatures.

PROGRAM GOALS

Molybdenum Alloy-Mo-.5Ti-.08Zr (TZM)

Development of braze alloys and techniques for brazing below the recrystallization temperature of TZM, with joint remelt capability up to 3300F.

Development of braze alloys and techniques for brazing closed cell honeycomb panels which will withstand a single exposure at 3000F for one hour with a 1.2 psi flatwise tensile stress on the panel face sheets.

Determination of braze system - coating compatibility under an exposure of one hour at 3000F in a 1.2 psi air atmosphere.

Comparison of the performance of the best available diffusion bonded panels with brazed panels during an hour exposure at 3000F with a 1.2 psi flatwise tensile stress on the panel face sheets.

Demonstration of the manufacturing applicability of the brazing alloys and techniques developed during the program, using the Nortobraze process.(*)

Tantalum Alloys - Ta-10W,Ta-8W-2Hf,Ta-30Cb-7.5V

Development of braze alloys and techniques for brazing in the 2000 - 3150F range with a 3800F joint remelt temperature.

Development of braze alloys and techniques for brazing closed cell honeycomb panels which will withstand a one-hour exposure at 2500F - 3500F with a 1.2 psi flatwise tensile stress on the panel face sheets. A temperature of 3500F is required for the Ta-10W and Ta-8W-2Hf alloys and a temperature of 2500F - 3000F is required for the Ta-30Cb-7.5V alloy.

Determination of braze system - coating compatibility under conditions of one hour at 2500F - 3500F in a 1.2 psi air atmosphere.

Development of conventional braze alloys which flow 200F - 300F above the intended service temperatures and can meet the requirements of goals two and three.

(*) Patented quartz lamp brazing process developed by Northrop Norair.

II RESULTS

LITERATURE SURVEY

Literature surveys were conducted through the Defense Metals Information Center and the Defense Documentation Center. The subjects searched include brazing approaches and techniques, refractory alloy brazing, oxidation protective coatings for molybdenum and tantalum, and phase diagrams of potential braze systems.

Brazing of refractory alloys for high temperature service, and protective coating of tantalum were found to be in relatively early stages of development; only limited information was available. The following discussion is a summary and analysis of the available information as it applies to this program.

Molybdenum Brazing

Thermal Embrittlement

It is well known that molybdenum alloys can be seriously embrittled by thermal exposures which produce recrystallization[1]. Therefore, a brazing study on molybdenum must consider the effects of brazing thermal exposures on recrystallization and embrittlement behavior.

Recent studies have shown that the recrystallization temperature ranges for .011 inch and .002 inch Mo-.5Ti-.08Zr (TZM) are approximately 2400F-2700F and 2100F - 2500F respectively for a six minute exposure at temperature [2,3]. The lower recrystallization resistance of the .002 inch foil could be the controlling factor in establishing a maximum brazing temperature for TZM honeycomb structures.

The same investigations also showed that recrystallization per se did not cause severe embrittlement of .011 inch TZM and .010 inch Mo-.5Ti. Small amounts of recrystallization (5-15 percent) produced a slight degree of embrittlement based on bend transition temperature data. Increasing amounts of recrystallization up to at least 80 percent produced no additional embrittlement. However, once recrystallization was essentially completed and substantial grain growth occurred, severe embrittlement was observed.

Bend test data indicated that .002 inch TZM foil in the post-recrystallized condition possessed substantially better bend ductility than .011 inch TZM sheet in the same condition. This may have resulted from the higher degree of biaxiality for the sheet versus foil.

These observations suggest several practical implications. First, brazing cycles which produce recrystallization but no appreciable grain growth may be tolerated with respect to ductility. Secondly, it may be possible to base brazing cycles on the higher recrystallization behavior of the TZM sheet rather than the foil and still maintain adequate ductility. Both of these factors permit brazing temperatures as high as 2600F rather than 2100F based on a criterion of 0 percent maximum recrystallization of the foil.

It has been shown that a Larson-Miller type time-temperature parameter could accurately predict recrystallization behavior of TZM sheet exposed to a wide range of single thermal exposures[3]. In addition, the parameter can be used to predict recrystallization behavior for multiple exposures at a single temperature. However, double

thermal exposures using two different times and temperatures produced a greater amount of recrystallization than predicted by the parameter. A correction factor applied to the parameter was found to provide an approximate correlation between recrystallization behavior and such multiple thermal exposures.

The above approach can be used to advantage in this program to establish maximum allowable brazing temperatures. In addition, the time-temperature parameter can be used to establish the maximum allowable thermal exposure for all thermal cycles required in the brazing fabrication process. The post braze thermal cycles could include a diffusion heat treatment and an oxidation protective coating cycle.

Taking into account probable post braze thermal cycles, it appears that a one-minute braze cycle at temperatures to 2400F could be employed for brazing TZM honeycomb panels. This braze cycle, together with post braze thermal cycle, should be compatible with a satisfactory level of panel ductility.

Conventional Brazing

A number of investigations[2,4,5,6,7,8,9] have studied the use of precious metals, iron, nickel, and cobalt alloys for brazing molybdenum. These fillers have been considered for conventional brazing as well as for approaches aimed at increased joint remelt temperatures. Conventional brazing is defined as brazing with a filler possessing a solidus temperature at least 200F above the intended service temperature.

The reported applicability of these systems varied from good to poor. Phase diagram relationships indicate that most of these systems should form brittle intermetallic compounds and/or low melting phases with molybdenum at the filler metal-base metal interfaces. Thus, one would expect these systems to exhibit poor compatibility with molybdenum. However, in some cases the as-brazed joints were reported to be ductile. This may have resulted from rapid braze cycles which minimized base metal-braze alloy interaction. Regardless of this, actual applications of these joints would require a protective coating cycle followed by the service cycle. During these thermal exposures base metal-filler diffusion could occur to form the brittle or low melting phases predicted from phase diagrams.

Feinstein[7] studied the effects of elevated temperature diffusion treatments on molybdenum joints brazed with Au-17.5Ni. It was found that the diffusion treatments produced a Au-Ni-Mo intermetallic compound which reduced room temperature strength, presumably by joint embrittlement. McCown et al[9] reported that TZM joints brazed with a cobalt base alloy (Haynes 25) were embrittled by subsequent thermal exposures.

Young and Jones[10] studied solid state diffusion bonded joints between Mo-.5Ti and iron, nickel, and cobalt base alloys. Diffusion treatments resulted in intermetallic compound formation at the joint interfaces. The brittleness of the intermetallic zone was clearly indicated by the high interface microhardness data reported. Thus, the studies confirmed that iron, nickel, and cobalt-base alloys were not promising braze fillers for molybdenum.

Conventional brazing of molybdenum alloys has been investigated using higher temperature fillers which brazed in the 2900F - 3200F range [2,9,10]. The fillers were basically titanium alloys which were compatible with molydenum based on phase diagram relationships. These alloys formed ductile joints but the high brazing temperatures recrystallized and embrittled the base material. Thus use of titanium alloys eliminated the braze alloy-base metal compatibility problem, but substituted a recrystallization and embrittlement problem.

It appears that conventional brazing temperatures could be increased by using very short braze cycles. However, it is impractical to consider braze cycles of less than one minute at temperature. When the time-temperature parameter is used to determine the temperature that would produce 100 percent recrystallization of TZM during a one-minute braze cycle, a temperature of 2[illegible]00F for .01[illegible] inch TZM sheet and 2550F for .002 inch TZM foil was calculated. Thus, rapid cycle conventional brazing offered no promise for producing ductile TZM honeycomb panels for 3000F service.

High Remelt Temperature Brazing

Effective utilization of molybdenum brazements to 3000F requires the development of braze alloys which braze below the recrystallization temperature, but develop high remelt temperatures. This approach would retain base metal ductility in the as-fabricated condition and still permit high service temperatures.

"Diffusion sink" brazing is an approach for increasing braze joint remelt temperatures which has received some study. This concept involves the reaction of a braze alloy with the base material and/or refractory metal powder additions after proper filleting and flow have occurred. The reaction takes place during the braze cycle or during a post braze diffusion treatment at a lower temperature. The diffusion reaction results in a new alloy in the joint with a higher melting temperature.

McCown et al [9] investigated an 80(Ti-8.5Si) -20 molybdenum powder diffusion sink braze system for TZM. This system required a braze temperature of 2550F followed by a three hour diffusion treatment at 2200F. Joint remelt temperatures from 2950 to 3150F were reported on .010 inch gage tee joints lightly loaded to 2-6 psi tension on the legs of the tees. The data also showed the remelt temperature to decrease with increased joint loading. The braze joints were reported to be ductile, but the 2550F braze temperature was observed to be somewhat high from the standpoint of base metal recrystallization. In another investigation of the Ti-8.5Si alloy[11] it was concluded that the 2550F braze temperature of this alloy resulted in recrystallization of the TZM. This study raised some questions regarding the ductility of the alloy as well.

Hagill, et al[12] investigated a Ti-13.5Cr-8.5Si alloy, which was reported to possess excellent potential for brazing TZM[9]. Tee joints were brazed with the braze alloy alone and with a columbium powder diffusion sink addition. The braze alloy melted at approximately 2380F and exhibited good filleting and flow at 2430F. The columbium diffusion sink and a diffusion treatment of one hour at 2200F produced relatively mild increases in remelt temperature. This may have resulted from limited diffusion reaction produced by the diffusion treatment employed.

The most important conclusions of this work were that the braze alloy exhibited marginal ductility and the columbium powder additions did not improve ductility. In addition, the diffusion treatment produced a significant increase in the microhardness of the braze alloy and presumably a decrease in ductility.

A "reactive brazing" concept has been considered for producing high remelt temperatures on refractory alloy brazements[13]. Reactive brazing is based on using a braze alloy containing a strong melting temperature depressant[13]. The depressant is selected to react with the base material or powder additions to form a high melting intermetallic compound during a post-braze diffusion treatment. By removing the depressant in this manner, the joint remelt temperature is increased. As an example of this approach a proprietary alloy designated RCN-15 was used to braze .006 inch TZM tee joints at 2150F[11]. A subsequent five hour diffusion treatment at 2200F produced a remelt temperature of 2980F with a 1000 psi stress on the base material. The joints were reported to be ductile at room temperature based on bending the .006 inch leg of the tee at some distance from the fillet. This produced substantial

deformation of the base material but little deformation of the joint.

A reactive Pt-B braze system for brazing tungsten was reported to produce lap joint remelt temperatures approaching 4000F under a 21.5 psi shear stress[11]. This system appeared to offer promise for brazing molybdenum; however, McCown et al[9] evaluated the alloy on TZM tee joints and found it extremely brittle in the as-brazed condition.

The concept of reactive brazing offers potential for increasing joint remelt temperatures. Successful application of this concept appears highly dependent upon controlling the intermetallic compound reaction to form discreet particles. If continuous intermetallic compound films are present in the grain boundaries or along the base metal-filler interfaces, joint ductility could be seriously impaired.

Tantalum Brazing

Thermal Embrittlement

Available information[15,16,17] indicates that tantalum alloys are not severly embrittled by recrystallization and grain growth. This behavior is in sharp contrast to that reported for molybdenum alloys. If reduced strengths are acceptable, there appears to be no metallurgical reason why tantalum alloys could not be brazed at temperatures approaching 4000F to obtain service to 3500F. However, brazing temperatures in excess of 3200F would present severe manufacturing and equipment problems. Therefore, brazing to obtain high remelt temperatures, as well as conventional brazing, is considered highly desirable.

Conventional Brazing

Very little information has been reported on brazing tantalum alloys for high temperature service. Young and Jones[10,18], concentrated primarily on development of conventional braze alloys for columbium and tungsten. Some of these systems appeared applicable to tantalum brazing. The V-35Cb and Ti30V braze alloys developed for columbium were used to braze Ta-30Cb-5V joints. Excellent filleting and flow were reported and it was concluded that these alloys offered potential for tantalum brazing.

In the same investigations several columbium-base alloys were identified for conventional brazing of tungsten for service to 3500F. Of these, a Cb-2.2B alloy appears to offer excellent potential for conventional brazing of tantalum alloys for 3500F service.

The filleting and flow properties of several potential braze alloys were determined on pure tantalum tee joints[19]. No significant differences in braze alloy behavior were noted between vacuum or argon brazing atmospheres. Pure titanium and Ti-30V exhibited poor filleting and flow. A Ti-13V-11Cr-3Al alloy exhibited fair filleting and flow while excellent results were observed with Ti-30Cr and V-20Ti.

High Remelt Temperature Brazing

No references were found on brazing of tantalum to develop high remelt temperatures. However, the diffusion sink and reactive brazing concepts discussed for molybdenum are applicable to tantalum alloys as well.

Other Brazing Approaches

Investigations have been conducted to develop high remelt temperatures by evaporation of a volatile melting temperature depressant from the braze alloy[20,21]. This work was conducted using nickel-base braze alloys but the concept is applicable to

brazing in general. The approach offers excellent potential but is subject to joint geometry limitations. Since closed cell honeycomb structures are to be considered in this program, a volatile element cannot be removed. Therefore, this approach will not be considered further.

An exothermic brazing approach is under investigation for brazing refractory alloys at temperatures up to 3100F[22]. This concept is actually a conventional brazing approach using an exothermic reaction as the heat source rather than conventional heating equipment. The process offers distinct advantages from the equipment standpoint. However, it also poses serious problems with regard to temperature control, entrapment of reaction products in the joints, and compatibility of reaction products with the base materials. These problems could complicate the development of braze systems on this program and therefore exothermic brazing will not be utilized.

Oxidation Protective Coatings

Oxidation protective coatings for brazed molybdenum and tantalum joints should be compatible with the braze joints as well as the base materials. A recent summary of coating research effort[23] indicates that little attention has been directed to this area. This gap in fundamental information has made it difficult to consider coating compatibility as one parameter of braze alloy development. Estimates of braze alloy-coating compatibility should be possible from phase diagram and thermodynamic data.

Molybdenum Coating

Numerous studies have been devoted to development of coatings for molybdenum. Most of the coatings interacted with the base material. Therefore, substrate thickness below .020 - .030 inch becomes an important variable where thin gage TZM honeycomb structures are involved.

An investigation is presently in progress to determine applicability of available coatings to .006 inch TZM foils[24]. A number of coatings are being screened and the following coatings have been found to offer promise for advanced evaluation.

1. Chance Vought - 2 cycle Si-(Cr-B), pack cementation
2. General Telephone and Electronics - 70Sn-25Al-5Mo, spray and sinter coating
3. Pfaudler - PRF-6, pack cementation
4. Chromalloy - W-3, pack cementation

The results of this evaluation should provide a good basis for TZM coating selection.

Hugill et al[12] found that several titanium-base braze alloys for TZM were not compatible with the Pfaudler PRF-6 coating. The braze alloys were attacked during the coating cycle. Subsequent oxidation tests in air showed the coating to provide little protection to the braze alloys. This limited data suggests that titanium-base braze alloys, in general, may not be compatible with pack cementation coatings.

Tantalum Coating

At present only two coatings have received concentrated attention for tantalum protection. These are the Sn-Al type[25,26] and the silicide type[27]. The Sn-Al type coating appears to be useful to approximately 3400F in air. Maximum useful temperature decreases in rarified air atmospheres due to coating evaporation. Columbium and vanadium-containing tantalum alloys were found to be compatible with the coating. Alloying elements which form oxides thermodynamically more stable than Al_2O_3 are detrimental to oxidation resistance in amounts greater than 5-10 percent.

Zirconium and hafnium are prime examples.

The silicide type coating appears to be useful to approximately 3000F in air. Composition of the substrate significantly affects coating performance. Tunsten, molybdenum, and vanadium improve the oxidation protection at high temperatures. Vanadium is particularly effective in enhancing low and high temperature oxidation protection. Hafnium appears to be somewhat detrimental to coating behavior.

No information is available on braze alloy-coating compatibility. Nevertheless, the data on effects of base metal alloying elements on coating performance provides a basis for estimating possible braze alloy-coating interactions.

Phase Diagram Data

Molybdenum Braze Systems

Four compilations were found to contain most of the available phase diagrams of interest [28,29,30,31]. These data show that W, Ta, Cb, Cr, V and Ti are compatible with molybdenum based on a criterion of complete solid solubility. However, the melting temperatures of W, Ta, and Cb are too high to consider them as braze alloy matrices. The brittle behavior of chromium precluded its consideration as a braze alloy matrix.

Titanium and vanadium are promising braze alloy matrices with titanium offering the greatest potential for the following reasons:

1. Titanium exhibits a lower melting temperature than vanadium.
2. More phase diagram data is available for titanium systems than vanadium systems.
3. The melting temperature of titanium can be more easily depressed to the desired 2000F - 2300F range.

Since titanium melts at 3050F, it is necessary to reduce the melting temperature by alloying. The most potent melting temperature depressants for titanium are Fe, Ni, Co, Cu, Mn, Si, Cr, Zr, and Be. Very limited data is available on the Ti - Be system. With the exception of Cr, these solute elements exhibit limited solid solubility in molybdenum. No elements were found which are both compatible with molybdenum and able to depress the melting temperature of titanium to the desired range. Consequently, the formulation of titanium-base braze alloys requires a consideration and balance between the following factors:

1. The quantity of depressant required to obtain the desired melting temperature.
2. The influence of the depressant on braze alloy ducti ty.
3. Phase relationships in the Ti - depressant (s) - Mo system with respect to intermetallic compound and low melting phase formation.
4. The influence of diffusion sinks on phase relationships, ductility and melting temperature of the braze alloy-base metal - diffusion sink system.

From phase diagram data[28] it appears that binary alloys of titanium containing Fe, Ni, Co, Cu, Mn, and possibly Be could be formulated to melt within the desired range. However, relatively large solute additions are required. These additions could seriously reduce ductility.

An investigation of Ti - Fe alloys indicated that iron levels well below those required to reach the desired melting range produced serious embrittlement[32].

Several alloys from the Ti-Fe-Mn system were also evaluated. Alloy selection was based on the liquidus data of Murakami et al[33]. It was found that alloys which melted within the desired temperature range were very brittle. The embrittling effects of Mn and Fe were quite similar. Therefore, the Ti-Fe and Ti-Fe-Mn systems offer limited potential as braze alloys.

The influence of Co, Ni, and Cu on ductility of titanium is not known at the levels of interest. Of these elements, Cu appears least promising because it is not as strong a melting temperature depressant as Co and Ni. Therefore, the Ti-Co-Cr and Ti-Ni-Cr systems offer potential because a portion of the Co and Ni could be replaced with Cr which is compatible with molybdenum. Liquidus isotherms in the Ti-Cr-Ni system have been developed as shown in Figure 1. It seems reasonable to assume that the form of the liquidus isotherms for the Ti-Cr-Co system are quite similar.

The Ti-Fe-Cr system appears to offer potential as a braze alloy if the Fe content can be held at low levels to minimize embrittlement. Some available data on solidus temperatures in the Ti-Cr-Fe system[34] offered a basis for alloy formulation.

Data has been reported on liquidus isotherms for the Ti-Cr-Mo system[35]. The data indicates that a Ti-Cr braze alloy offers excellent remelt potential using the diffusion sink brazing approach with molybdenum as the sink. However, the minimum melting temperature of alloys in the Ti-Cr system is approximately 2550F.

A Ti-13.5Cr-8.5Si alloy has been suggested for brazing TZM[9]. The liquidus temperature of the alloy is approximately 2400F. An estimate of the liquidus temperatures in Ti-Cr-Si system indicates that approximately 2400F is the minimum melting temperature of potential alloys. Substitution of Ni for Cr in this system offers potential for lower melting alloys. The estimated liquidus temperatures for the Ti - rich corner of the Ti-Ni-Si system are shown in Figure 2.

Binary phase diagrams indicate that nickel is a potent melting temperature depressant for both titanium and zirconium. In addition, titanium and zirconium are compatible. Therefore, the Ti-Zr-Ni system appears attractive from the standpoint of melting temperature and ductility.

A Ti-48Zr-4Be alloy was evaluated as a braze alloy for TZM[9]. This system was noted to be extremely brittle. Since the alloying behavior of Be with Zr and Ti is similar, it appears that the lack of ductility would extend to Ti-Be alloys. It is estimated that a minimum of 2 percent Be is required to depress the melting temperature of titanium to the desired range. Alloy ductility at this beryllium level is highly questionable.

Solid state phase relationships in the Ti-Zr-V system have been investigated[36]. Further studies have determined the ductility and melting temperatures of a number of alloys in this system[10]. These data were employed to estimate the liquidus isotherms shown in Figure 3. This system appears very attractive in that a wide range of melting temperatures is possible.

Zirconium exhibits limited solubility in molybdenum and a $ZrMo_2$ intermetallic compound. Limited data on the Mo-Ti-Zr phase diagram[31] showed that Ti suppresses formation of $ZrMo_2$. Therefore consideration of a Ti-Zr-V braze alloy for TZM appears justified. However, the alloy must be formulated with the lowest Zr content and highest Ti content consistent with melting temperature requirements.

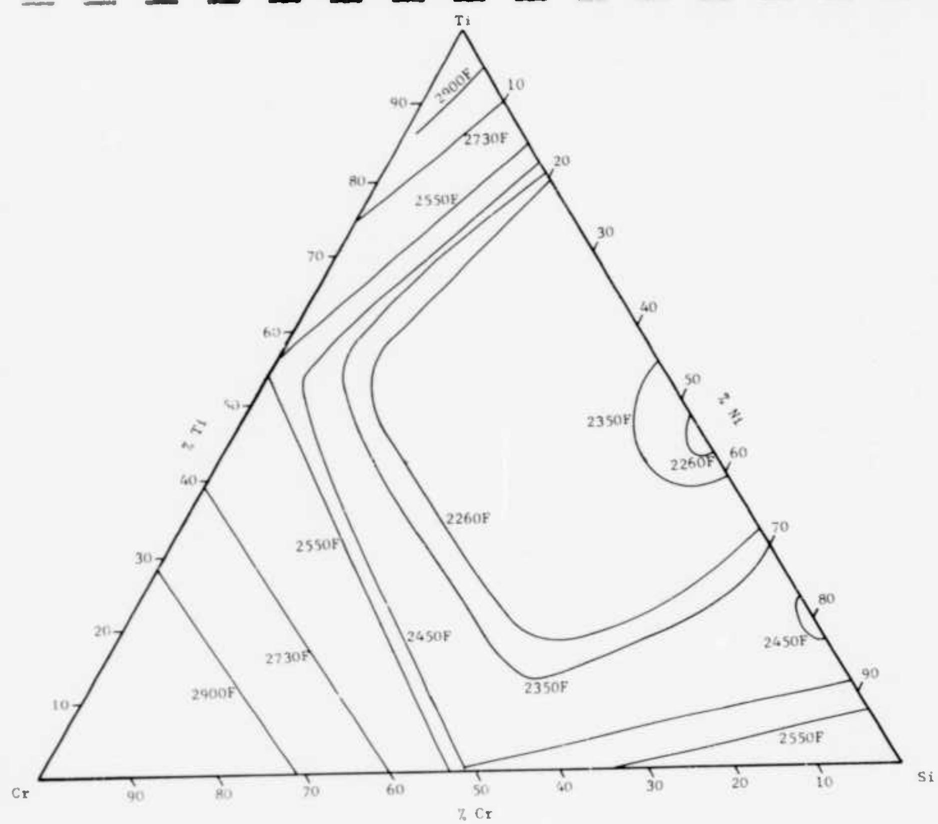


FIGURE 1 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-Cr-Ni SYSTEM

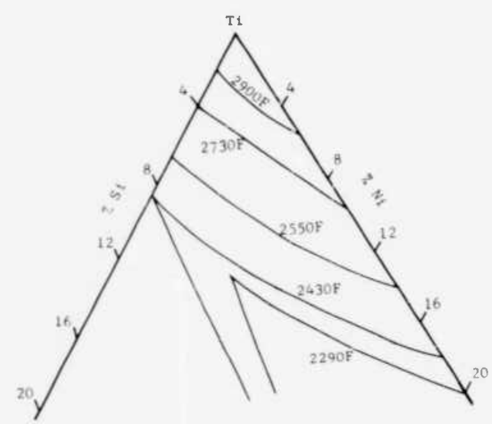


FIGURE 2 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-RICH CORNER OF THE Ti-Ni-Si SYSTEM

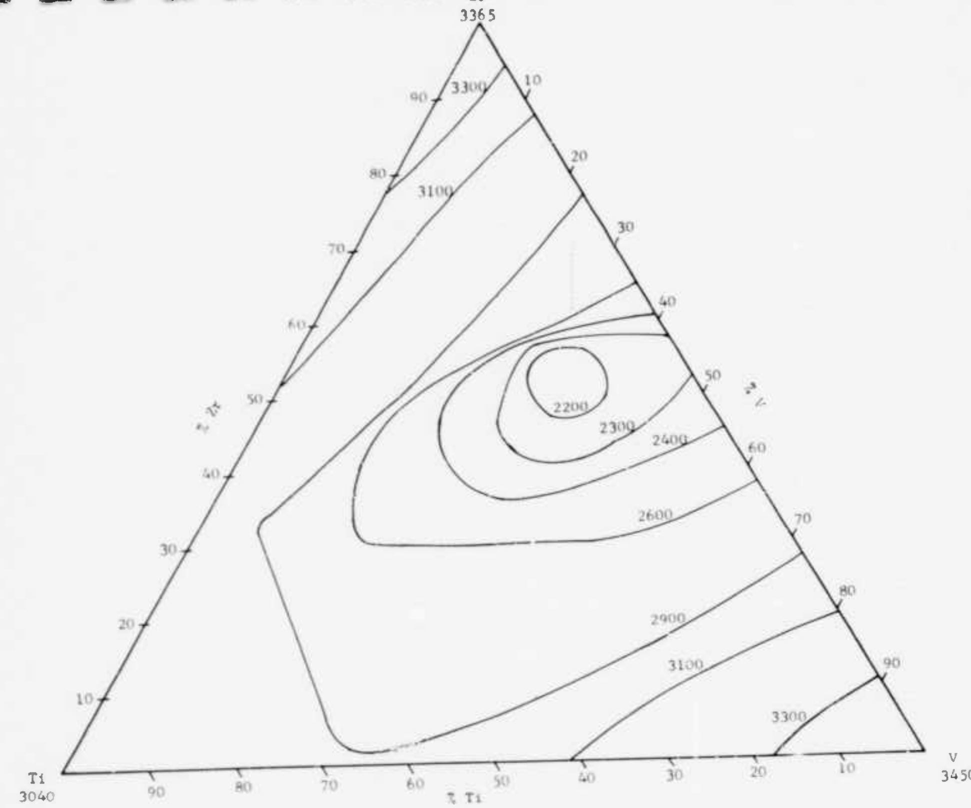


FIGURE 3 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr SYSTEM

The Ti-V-Zr system offers possibilities for reactive brazing. The phase diagram of Figure 3 shows that if Zr and/or V can be preferentially removed from the alloy, the liquidus temperature will be increased. These elements all show a high negative free energy of formation for high melting carbides and borides. If there are distinct differences in reaction rates, it may be possible to selectively form Zr and V compounds in preference to Ti compounds.

Incorporating the boron and/or carbon powders in the diffusion sink powder offers an attractive approach for adding these elements. This should result in formation of discreet boride and/or carbide particles rather than continuous films.

Limited data on melting temperatures and ductility of Zr-V-Cb alloys has been reported[10]. This alloy system offers some promise for developing TZM braze alloys.

Selection of optimum diffusion sinks for the above mentioned braze alloy systems required consideration of the following points.

1. Metallurgical compatibility of the diffusion sink with the base material and braze alloy.
2. Potential remelt temperature increase.
3. The quantity of diffusion sink powder that could be placed at fillet areas without inhibiting braze alloy filleting and flow.

The most logical diffusion sinks for the above systems are the refractory metals W, Ta, Cb, and Mo. All of these elements are compatible with Mo. However, W can be eliminated because of its brittle behavior and lack of compatibility with titanium. Tantalum is promising because it exhibits a high melting temperature, good ductility and high density. High density is advantageous in permitting larger sink additions to the fillets on a weight percentage basis.

The Ta, Mo, and Cb binary phase diagrams with titanium indicate that Ta and Mo offer the greatest potential for increasing the remelt temperature of pure Ti. However, it is difficult to predict remelt potential and phase relationships in the multi-component systems represented by the braze alloy-diffusion sink systems. A major unknown is the quantity of diffusion sink powder that can be placed at fillets without impeding braze alloy flow. In view of these complex considerations it appears that selection of optimum diffusion sinks required detailed experimental effort.

Tantalum Braze Systems

Phase diagram data [28,29,30,31] show that W, Mo, and Cb are compatible with Ta based on a criterion of complete solid solubility. The elements Ti, V, Zr, and Hf are compatible with Ta at high temperatures but the systems show solid state transformations over broad composition ranges at lower temperatures. The transformation in the Ti-Ta system is the allotropic titanium transformation which is not expected to cause embrittlement. However, the transformations in the V, Zr, and Hf binaries with Ta could cause embrittlement. It has been reported[18] that a Zr-34 Ta alloy is brittle in the as-cast condition.

The elements W, Ta, Mo, Cb, and Hf appear applicable as conventional braze alloy matrices for 3500F service. However, W and Mo can be eliminated because of their limited ductility. Hafnium is eliminated because it is not compatible with tantalum coatings. Thus Cb and Ta offer the greatest potential as braze alloy matrices.

A review of phase diagram data indicated that Ti and V are the most promising melting temperature depressants for Cb and Ta. It has been reported that Ta-base alloys with Ti and V are somewhat difficult to arc-melt due to excessive volatilization of the solute elements[10]. Since Cb melts at a much lower temperature than Ta, Cb-base alloys with Ti and V appear more promising. In addition, some data are available on ductility and melting temperatures of these alloy systems[10].

The Ta-B and Cb-B systems also appear promising for conventional brazing. The published phase diagram for the Cb-B system[30] shows a eutectic at approximately 2950F and 2.2 percent B. Data by Young and Jones[10] indicates that the eutectic temperature is approximately 3800F - 4000F. It was also noted that Cb-B alloys containing up to 2.2 percent B are ductile. If this data is correct, the Cb-B system offers promise for conventional brazing.

The published Ta-B phase diagram[30] shows a eutectic at approximately 3300F and 1.3 percent B. One would expect the Ta-B eutectic to melt at a higher temperature than the Cb-B eutectic. Therefore, if the data on the Cb-B system by Young and Jones is correct, the accuracy of the Ta-B phase diagram may be questionable. It appears that some experimental evaluation of these systems is necessary to establish melting temperatures. If the melting temperature is above 2700F, the systems offer excellent potential for conventional brazing. If the temperatures reported in the published phase diagrams are correct, these systems may offer promise for diffusion sink brazing at lower temperatures.

Titanium, V, and Zr were found to offer the most promise as braze alloy matrices for diffusion sink brazing below 3200F. A revised diagram of the Ta-Zr system[37] shows that Ta exhibits a very mild effect on the melting temperature of Zr. Therefore, Zr was eliminated as a braze alloy matrix. The applicability of V as a matrix is questionable due to possible embrittlement by formation of TaV_2. Thus, Ti is judged to be the most promising matrix for diffusion sink braze alloys.

The most promising melting point depressants for Ti are V, Zr, Cr, Fe, Si and Mn. Only V and Zr are completely compatible with Ti. Manganese was eliminated because it was similar in behavior to Fe but not as potent a depressant.

The binaries Ti-30V and Ti-40Zr represent the minimum melting temperatures in these systems and exhibit good potential as basic braze alloys. However, ternary alloy additions to Ti-30V are considered necessary to improve filleting and flow. These additions will reduce the melting temperature further.

The Ti-V-Si system appears promising particularly from the standpoint of improved filleting and flow. The estimated liquidus temperatures for the Ti-V-Si system are shown in a portion of Figure 4. This data shows that Si will depress the melting temperature of the Ti-V system.

Binary phase diagram data show that Fe is a good melting temperature depressant for Ti and a fair depressant for V. In addition, V exhibits reasonably high solid solubility for Fe. Thus, the Ti-V-Fe system is attractive for lowering the melting temperature of the Ti-V system. The influence of Fe in filleting and flow of the Ti-V system is unknown. However, it is possible that Fe could improve alloy behavior.

The Zr-V-Ti system discussed previously for brazing molybdenum also offers potential for brazing tantalum. This system has possibilities for reactive as well as diffusion sink brazing using the principles discussed earlier. Information obtained on the binary phase diagrams of Cb and Ta with iridium, rhodium, platinum and

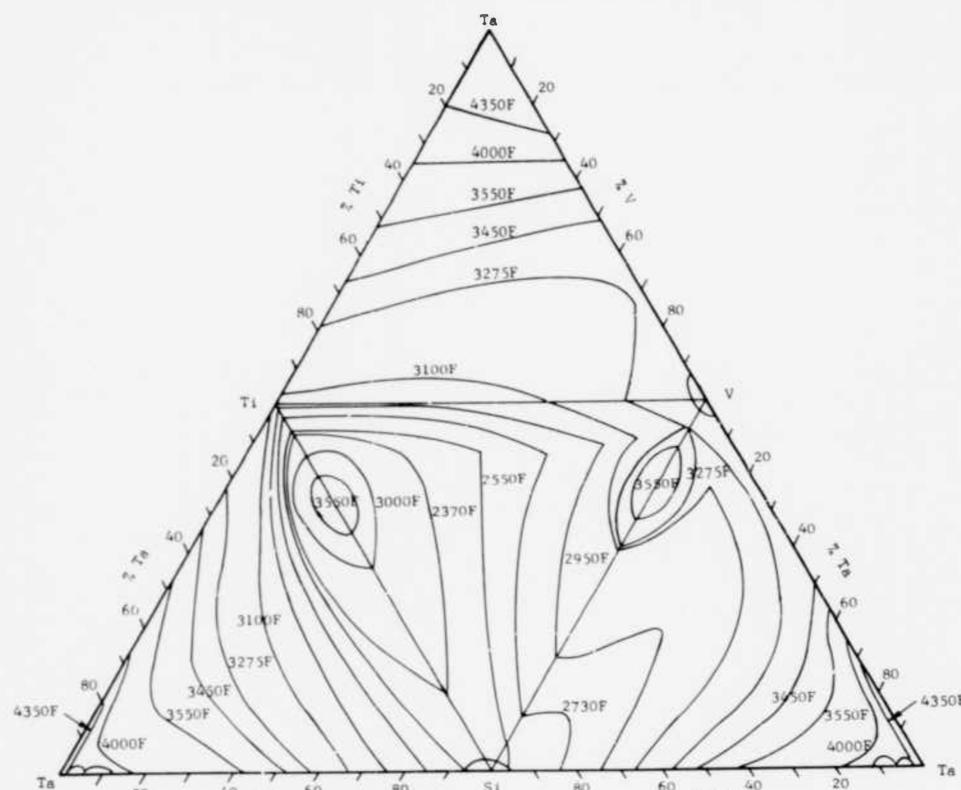


FIGURE 4 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Si-Ta SYSTEM

palladium[38] show these systems with melting temperatures of approximately 3300F or lower. However, the diagrams show that Cb or Ta diffusion sink additions within relatively broad ranges result in sigma phase formation and embrittlement. Therefore these systems offer limited potential as braze alloys.

The Ta-B and Cb-B systems discussed in relation to conventional braze alloys offer possibilities for diffusion sink brazing. Determination of melting temperatures in these systems is necessary to confirm their applicability.

The selection of optimum diffusion sinks for tantalum is subject to the same considerations mentioned previously for molybdenum. The diffusion sink remelt potential of the Ti-Zr-V system was estimated for Cb and Ta sink additions. The estimated ternary liquidus surfaces of the Ti-Zr-V-Cb and Ti-Zr-V-Ta quaternary tetrahdrons were estimated and projected on a plane. The results are shown in Figures 5 and 6.

From these figures it can be seen that small diffusion sink additions of Ta or Cb to the Ti-Zr-V ternary produce relatively mild increases in remelt temperature. However, larger additions could produce proportionally greater increases.

Portions of Figure 5 and 6 show similar trends for Cb and Ta additions to the Ti-Zr and Ti-V systems. The estimated liquidus temperatures for the Ti-V-Si-Ta system shown in Figure 4 also exhibit this trend.

Resume' of Survey

On the basis of the extensive literature survey, experience and limited experimental data the following highlights may be noted with regard to refractory alloy brazing.

1. Brazing temperatures for TZM honeycomb panels should be limited to 2400F (1 minute exposure) to retain optimum base metal ductility.

2. Brazing temperatures as high as 2600F (1 minute exposure) for TZM honeycomb panels may result in acceptable base metal ductility.

3. Conventional brazing of TZM does not produce ductile honeycomb panels for service to 3000F.

4. Tantalum alloys are not seriously embrittled by high temperature exposures. Therefore conventional brazing for service to 3500F is metallurgically acceptable.

5. Brazing fillers for molybdenum and tantalum alloys should be based on alloys exhibiting solid solubility in the base metal to assure joint ductility and metallurgical compatibility.

6. Diffusion sink and reactive brazing are the most promising methods for brazing molybdenum and tantalum alloys to develop high remelt temperatures and thus high service temperatures.

7. No reasonably suitable braze fillers for molybdenum and tantalum alloys have been developed to date for the service temperatures considered in this program.

8. In general Ti - base alloys offer the greatest potential for brazing TZM.

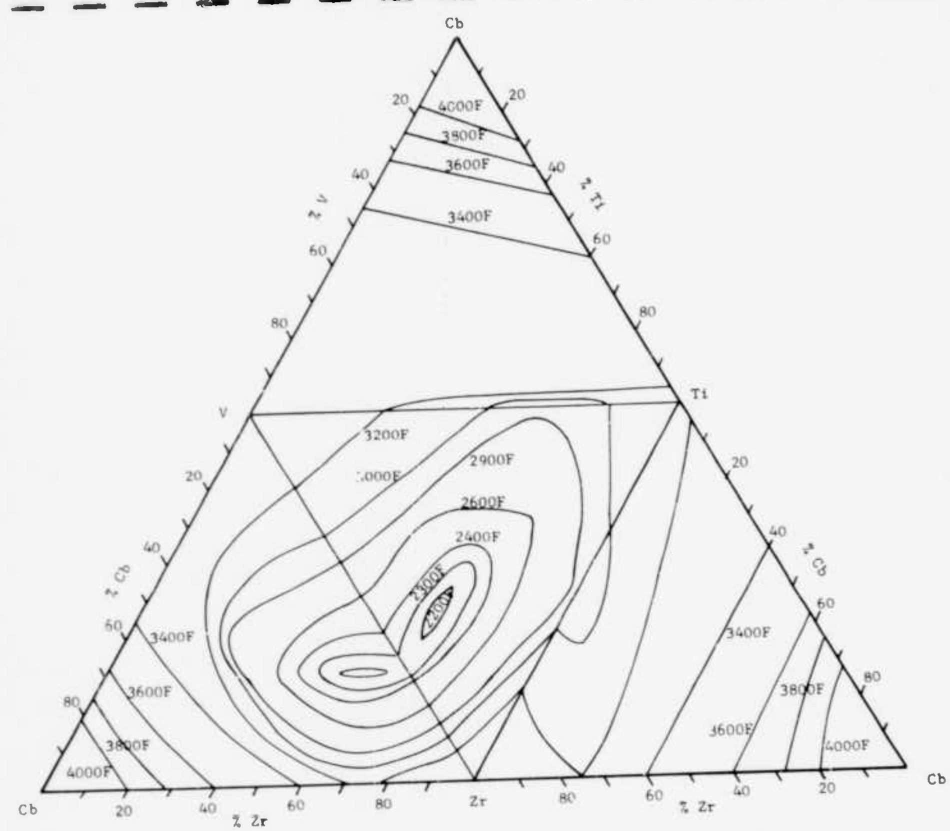


FIGURE 5 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr-Cb SYSTEM

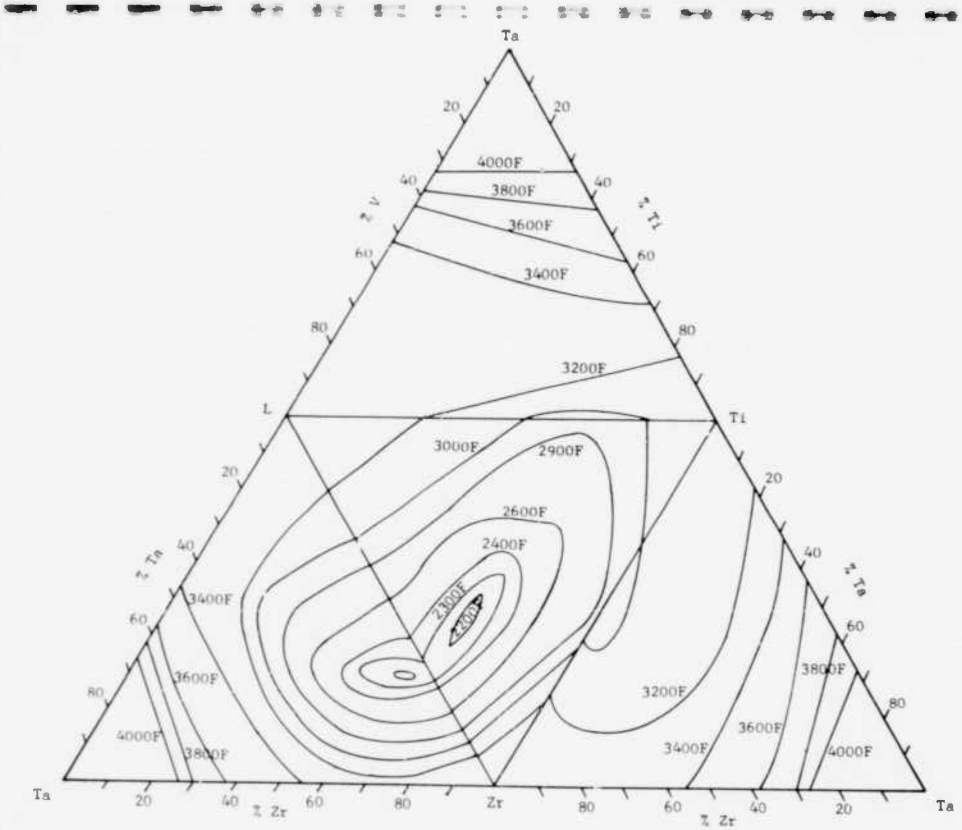


FIGURE 6 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr-Ta SYSTEM

9. The following alloy systems appear most promising for molybdenum braze alloy development:

Ti-Co	Ti-Cr
Ti-Ni	Ti-Ni-Si
Ti-Co-Cr	Ti-Zr-Vi
Ti-Ni-Cr	Ti-Zr-V
Ti-Fe-Cr	Zr-V-Cb

10. The most promising diffusion sink elements are Ta, Cb, and Mo.

11. The following alloy systems offer the greatest potential for conventional brazing of tantalum:

Cb-V	Ta-B
Cb-Ti	Cb-B

12. The following alloy systems offer the greatest potential for high remelt temperature brazing of tantalum.

Ti-Zr	Ti-V-Fe-(Cb,Ta, or Mo)
Ti-V-Si	Ti-V-Si-(Cb,Ta, or Mo)
Ti-V-Fe	Ti-Zr- (Cb,Ta, or Mo)
Zr-V-Ti	
Ta-B	
Cb-B	

13. Several promising high temperature coatings are available for base metal protection of TZM and Ta-10W alloys.

14. Coating/braze alloy compatibility problems may exist for titanium base braze alloys on TZM using pack cementation type coatings.

15. No data on coating/braze alloy compatibility on Ta base alloys was found.

BRAZE SYSTEM DEVELOPMENT

Experimental braze alloy compositions were produced by conventional button arc melting in a 400 mm high purity argon atmosphere. Each alloy was melted six times to insure homogeneity. The alloys were weighed before and after melting and the compositions assumed to be correct if no appreciable weight changes were noted. A qualitative measure of alloy ductility was obtained by chiselling a chip off the button. The following designations and their definitions were used to rate ductility

Ductile - Substantial chip curling or deformation.
Slightly Ductile- Some chip curling or deformation.
Brittle - No visible deformation.
Very brittle - Button fractured when struck with chisel.

It is believed that alloys rated ductile or slightly ductile possess adequate ductility for use as braze alloys. Applicability of alloys rated brittle is questionable while those rated very brittle are considered unsuitable.

The liquidus temperatures of the alloys were determined from a section of each button. The sections were placed on a refractory metal sheet, heated in a 300 mm argon atmosphere and the liquidus temperature determined by visual observation. Temperatures to 3100F were measured by Pt/Pt-10Rh thermocouples and W/W-26Re couples were employed at higher temperatures. Accuracy of the liquidus determinations is estimated to be within ±20F to 3100F and ±30F at higher temperatures.

The braze alloy buttons were alloyed with suitable refractory metals to simulate diffusion sink additions. It was arbitrarily assumed that the base metal would contribute a 10 wt. percent diffusion sink addition to the braze fillet. This is a very conservative figure. If complete base metal-braze alloy diffusion occurs between a .002 inch honeycomb-.010 inch face sheet joint brazed with .010 inch radius fillets, the fillets would contain approximately 60 percent base metal.

A diffusion sink powder addition representing 15 percent of the braze fillet weight was employed. Thus, the diffusion sink additions to the braze alloy were standardized at 10 percent base metal - 15 percent diffusion sink powder.

The ductility and liquidus temperatures of these systems were determined in the same manner employed on the original buttons. A summary of the alloy compositions, liquidus temperatures, and ductility ratings is given in Tables I and II.

The remelt temperatures produced by various diffusion sinks listed in these tables were obtained by additions of equal amounts of the various sinks.

In actual practice the remelt temperature obtained will depend upon (1) the remelt increase per unit wt. percent of diffusion sink added, and (2) the maximum amounts of various diffusion sink powders that can be incorporated in a joint without affecting braze alloy behavior. Several experiments may be necessary to determine this latter parameter. Therefore, the choice of diffusion sinks discussed in the following section may require modifications based on these experiments.

Molybdenum Braze Systems

The experimental results on the molybdenum braze systems are shown in Table I. The Ti-10Co-25Cr, Ti-13Fe-13Cr, Ti-10Ni-25Zr, and Zr-30V-20Cb braze alloys are eliminated from further consideration because they are either brittle or very brittle. A comparison between the Ti-20Co and Ti-21Ni shows the latter to exhibit a lower liquidus temperature and similar ductility. Therefore, the Ti-20Co alloy is eliminated. Similarly, the Ti-8Ni-7Si alloy is preferable to the Ti-7Ni-7Si modification.

TABLE I

MOLYBDENUM BRAZE SYSTEMS

Button No.	Composition Wt. %	Liquidus Temp. F	* Ductility	Increase in Liquidus Temp. F
26	Ti-20Co	2220	SD	
27	Ti-21Ni	2070	SD	
46	75(Ti-21Ni)-25Mo	2700	B	630
47	30(Ti-21Ni)-8Mo-12Ta	2490	B	420
29	Ti-10Co-25Cr	2340	VB	
28	Ti-10Ni-25Cr	2300	SD	
59	75(Ti-10Ni-25Cr)-15Mo-10Ta	2900	VB	600
60	75(Ti-10Ni-25Cr)-25Mo	3060	B	760
34	Ti-13Ni-15Cr	2290	SD	
49	75(Ti-13Ni-15Cr)-10Mo-15Ta	2745	B	455
48	75(Ti-13Ni-15Cr)-25Mo	2780	B	490
24	Ti-13Fe-13Cr	2420	B	
20	Ti-35Cr	2600	SD	
56	75(Ti-35Cr)-25Mo	3130	VB	530
57	75(Ti-35Cr)-10Mo-15Cb	2960	VB	360
36	75(Ti-35Cr)-25Ta	2740	B	140
90	Ti-7Ni-7Si	2320	SD	
45	Ti-8Ni-7Si	2250	SD	
50	75(Ti-8Ni-7Si)-25Mo	2690	B	440
58	75(Ti-8Ni-7Si)-10Mo-15Ta	2610	VB	360
30	Ti-10Ni-25Zr	2460	B	
31	Zr-30V-20Cb	2340	VB	
32	Ti-31V-38Zr	2370	D	
42	Ti-30V-40Zr	2335	D	
65	Ti-29V-42Zr	2340	D	
115	Ti-32V-43Zr	2220	D	
43	75(Ti-35V-36Zr)-25Mo	2960	SD	~560
35	75(Ti-35V-36Zr)-10Mo-15Cb	2810	SD	~410
86	Ti-35V-30Zr	2570	SD	
102	Ti-33V-33Zr	2480	SD-D	
93	75(Ti-35V-30Zr)-25Mo	3010	SD	440
94	75(Ti-35V-30Zr)-10Mo-15Ta	2990	SD	420

* D = Ductile B = Brittle
SD = Slightly Ductile VB = Very Brittle

TABLE II

TANTALUM BRAZE SYSTEMS

Button No.	Composition Wt. %	Liquidus Temp. F	* Ductility	Increase in Liquidus Temp. F
84	Cb-30Ti		D	
85	Cb-25V	~3950	D	
51	Ta-36V (as melted)		D	
51	Ta-36V (aged 45 min. at 2300F)		VB	
73	Ti-37Zr	2880	D	
75	75(Ti-37Zr)-10Ta-15Mo	3010	D	130
76	75(Ti-37Zr)-25Ta	3100	D	220
77	75[75(Ti-37Zr)-10Ta-15Mo]-25Ta	~3450	D	~570
78	75[75(Ti-37Zr)-25Ta]-25Ta	3110	D	230
92	75[75(Ti-37Zr)-10Ta-15Mo]-10Ta-15Mo	3320	SD	440
41	Ti-29V-2Si	2820	SD	
53	75(Ti-29V-2Si)-25Ta	3020	D	200
64	75(Ti-29V-2Si)-10Ta-15Cb	3020	D	200
138	75(Ti-29V-2Si)-10Ta-15Mo	3150	D	330
71	75[75(Ti-29V-2Si)-25Ta]-25Ta	3240	D	240
72	75[75(Ti-29V-2Si)-25Ta]-10Ta-15Mo	**3400	D	400+
44	Ti-27V-7Fe	2700	D	
54	75(Ti-27V-7Fe)-25Ta	2960	D	260
63	75(Ti-27V-7Fe)-10Ta-15Cb	2980	D	280
67	75[75(Ti-27V-7Fe)-25Ta]-25Ta (as melted)	3240	D	280
67	(aged 30 minutes at 2000F)		D	
70	75[75(Ti-27V-7Fe)-25Ta]-10Ta-15Mo	3320	B	360
42	Ti-30V-40Zr	2335	D	
52	75(Ti-30V-40Zr)-25Ta (as melted)	2745	SD	410
52	(aged 30 min. at 2000F)		SD	
61	75(Ti-30V-40Zr)-10Ta-15Cb	2790	SD	455
43	75(Ti-35V-36Zr)-25Mo	2960	SD	~560
81	75[75(Ti-30V-40Zr)-25Ta]-25Ta	3220	SD	465
82	75[75(Ti-35V-36Zr)-25Mo]-10Ta-15Mo	3320	B	360

* D- Ductile
SD-Slightly Ductile
B-Brittle
VB-Very Brittle

** Solidus Temperature

Several Ti-V-Zr alloys were formulated. The Ti-32V-43Zr composition (button 115) is most promising because it exhibits a low liquidus temperature and good ductility. Buttons 86 and 102 are higher melting Ti-V-Zr alloys for brazing above the recrystallization temperature of TZM core but below the recrystallization temperature of the TZM face sheets. Button 102 represents the preferred composition.

The Mo diffusion sink additions to the Ti-Ni, Ti-Ni-Cr, Ti-Cr, and Ti-Ni-Si braze alloys produce the largest liquidus temperature increase and minimum reduction in ductility. The Ti-10Ni-25Cr braze alloy shows the highest remelt potential of these systems and has been selected for evaluation on tee joints. Although the Ti-8Ni-7Si alloy exhibits less remelt potential, it is still considered attractive for two reasons. First, it is a lower melting modification of the Ti-8.5Si alloy which has shown large remelt temperature increases in brazing TZM[9]. Secondly, it represents an approach based on a metal-metalloid braze alloy.

The data for the Ti-V-Zr alloys presented in Tables I and II are based on diffusion sink brazing alone. A Mo diffusion sink addition to the lower melting Ti-V-Zr alloys produced the largest liquidus temperature increase. Another brazing approach with this alloy involves a combination of diffusion sink and reactive brazing using B and/or C additions. This approach cannot be evaluated by additions to alloy buttons but requires experiments on actual joint configurations. This is necessary because the B and/or C must be added to the diffusion sink powder as discreet particles to avoid embrittling compound films.

The higher melting Ti-35V-30Zr alloy shows somewhat less remelt potential than the lower melting modifications. Nevertheless, the alloy is still promising because the lower Zr and higher Ti contents will reduce the tendency for $ZrMo_2$ formation. Diffusion sink additions of Ta and Mo produce essentially equivalent increases in the liquidos temperature. Since Ta exhibits a higher density than Mo, it offers potential for placing more sink powder in a braze joint. Therefore, Ta has been selected as the diffusion sink for this braze alloy. This will permit later comparisons between Ta as a diffusion sink in this alloy versus Mo as a diffusion sink for the lower melting Ti-V-Zr braze alloy.

With the exception of the Ti-V-Zr alloys, diffusion sink additions reduce braze alloy ductility to the brittle or very brittle classifications. The systems rated brittle by the chisel test may still possess sufficient ductility for honeycomb brazing applications. The Rockwell C hardness of a number of alloys was measured to determine if (1) hardness could be correlated with chisel test ductility and (2) if there were any differences between systems rated brittle. Unfortunately, the hardness data showed poor correlation with ductility as measured by the chisel test.

A summary of the most promising TZM braze systems to be evaluated on tee joints is given in Table III. Estimates of the amount of diffusion sink required for a 3300F remelt temperature are also included. These estimates are based on the data of Table I and phase diagram considerations.

Tantalum Braze Systems

The data on the tantalum braze systems is shown in Table II. Evaluation of the Cb-30Ti and Cb-25V conventional braze alloys is in progress. Both alloys are ductile and the liquidus temperature of the latter is approximately 3950F.

TABLE III

FINAL BRAZE SYSTEMS

Braze Alloy	Liquidus Temp. F	Diffusion Sink Powder	Estimated % Diffusion Sink Required For Remelt Temperature of 3300F	3400F	3800F
T2M					
1. 43Zr-25Ti-32V	2220	Mo	45		
2. 43Zr-25Ti-32V	2220	Mo+BorC	45 (Mo alone)		
3. Ti-8Ni-7Si	2250	Mo	55		
4. Ti-25Cr-10Ni	2320	Mo	35		
5. 33Zr-34Ti-33V	2480	Ta	35		
Ta-10W					
6. 43Zr-25Ti-32V	2220	(a)		50 (Mo alone)	70 (Mo alone)
				45 (Cb alone)	70 (Cb alone)
7. Ti-27V-7Fe	2700	Ta		55	70
8. Ti-29V-2Si	2820	Ta or Mo		60 Ta	75 Ta
9. Ti-28Zr-15Mo-10Ta	3000	Ta		25	45
10. Ti-21.5V-1.5Si-25Ta	3020	Mo		30	50
11. To be determined					
12. Cb-25V	3950	none			
13 Cb-30Ti	3900	none			
14. To be determined					

(a) Mo or Cb+ B or C to be employed depending upon results from alloys 1 and 2

The Ta-36V alloy was prepared to determine compatibility of V-base braze alloys with Ta. The as-melted alloy exhibits a hardness of Rc 37 and is ductile. Aging 45 minutes at 2300F increased the hardness to Rc 53 and produces severe embrittlement. The as-melted alloy cooled rapidly enough to retain the high temperature solid solution. However, aging at 2300F resulted in transformation resulting in the formation of TaV_2 which was highly embrittling. Since coating cycles are carried out at temperatures where TaV_2 can form and embrittle the braze joints, further effort on the V-base braze alloys has been suspended.

A diffusion sink addition of Ta to the Ti-37Zr braze alloy produces a larger increase in liquidus temperature than a Mo addition. However, comparison of button 76 to 78 shows that the added Ta addition to 78 produces no further increase in the liquidus temperature. The 75 (Ti-37Zr)-10Ta-15 Mo braze alloy (button 75) has the highest remelt temperature. This system has been selected for evaluation on tee joints.

Diffusion sink additions of Ta and Cb produce equivalent increases in the liquidus temperature of the Ti-29V-2Si alloy. However, Ta is judged to be somewhat more promising because of its higher density. Comparison of button 71 to 72 shows that Mo is a more potent diffusion sink than Ta. A braze alloy of the composition of button 53 has the highest remelt temperature with a Mo diffusion sink. Therefore, this system has been selected for evaluation on tee joints.

The Ti-29V-2Si braze alloy has been selected also for tee joint evaluation because it exhibits an intermediate liquidus temperature. The 2% Si addition depressed the liquidus temperature of the Ti-V binary alloy by approximately 100F. A Mo or Ta diffusion sink will be employed with this braze alloy.

The liquidus temperature of the Ti-27V-7Fe is approximately 200F below the liquidus of the binary Ti-V alloy. Diffusion sink additions of Cb and Ta produce equivalent liquidus temperature increases. Mo additions lead to somewhat higher remelt temperatures but produce embrittlement (button 70). Comparison of button 72 to 67 shows that the Ti-V-Si-Ta system has greater remelt potential than the Ti-V-Fe-Ta system.

Because of its intermediate liquidus temperature the basic Ti-27V-7Fe braze alloy has been selected for tee joint evaluation. A Ta diffusion sink appears most promising. However, there is some question concerning the compatibility of Ta with the V in the braze alloy. Button 67 was aged 30 minutes at 2000F to determine if the system would be embrittled by TaV_2 formation. No change in Rc hardness or ductility was produced by the aging treatment. This data also indicates that the Ti-V-Si system is probably compatible with Ta from the standpoint of TaV_2 formation.

The Ti-V-Zr system was discussed in detail with reference to molybdenum brazing. The optimum composition appears to be Ti-32V-43Zr. This alloy will be evaluated for brazing Ta. However, final selection of the diffusion sink and reactive brazing additions will be based upon the results obtained with the same basic system applied to Mo brazing.

Braze alloys based on the Ti-V-Zr-Ta system may offer good remelt potential using the reactive and/or diffusion sink concepts with a Ti diffusion sink. This will be explored during the next reporting period.

Button 52 was aged 30 minutes at 2000F to determine compatibility of the Ti-Zr-V braze alloy with Ta. The aging treatment increased the hardness from Rc 12 to Rc 29 but the alloy remained ductile. Further analysis to determine the microstructural changes accompanying the hardness increase appears to be in order.

A summary of the most promising braze systems selected to date for tee joint evaluation is given in Table III. Estimates of the amounts of diffusion sink required for 3400F and 3800F remelt temperatures are also included. These estimates are based on the data of Table II and phase diagram considerations. The diffusion sink alloys may be categorized as low melting (2220F), intermediate melting (2700F- 2820F) and high melting (3000F). The final alloy selection for brazing Ta will be completed during the next reporting period.

Braze Alloy Preparation

Most of the braze alloys listed in Table III have been reduced to powder for evaluation on tee joints. To facilitate powdering, the braze alloys were embrittled by hydriding for approximately 30 minutes at 600F - 1000F using a hydrogen flow rate of 10 - 30 CFH. The hydrogen was pre-cleaned using a titanium chip getter operating at 1550F.

After hydriding, the alloys were crushed to -100 mesh powder in a steel mortar and pestle. Any iron contamination was removed by magnetic separation. Heating the hydrided powders to 1200F - 2000F in vacuum, removed the hydrogen and restored braze alloy ductility. This dehydriding procedure will be incorporated into the brazing cycles.

Pre-Braze Cleaning Procedures

Several nitric-hydrofluoric acid solutions were evaluated for pre-braze cleaning the Ta-10W alloy. A 25HF - 25HNO3 - $50H_2O$ solution proved most effective. The detailed cleaning procedure is recorded in Table IV along with typical weight lose data. The procedure was evaluated further by metallographic analysis for intergranular or localized attack, braze alloy flow tests, and etching weight loss data.

A TZM pre-braze cleaning procedure reported in the literature[12] was found to produce excellent results on the .013 inch TZM to be employed on this program. However, the .002 inch TZM foil for this program contained a surface contamination layer which was clearly visible after a recrystallization treatment as shown in Figure 7. Therefore, it was necessary to modify the cleaning procedure to remove about 20 percent of the original thickness of the foil. The cleaning procedures adopted for the sheet and foil are detailed in Table V along with typical etching weight loss data.

Powder Placement

The development of methods for placing diffusion sink powders on honeycomb specimens was based on the following assumptions.

1. Sink powder is undesirable between the edges of the core and the face sheets.
2. Sink powder should be placed only at the fillets and nodes of the core.
3. Braze alloys should be placed on the face sheets only.

A number of placement methods were investigated; the most promising method involved dipping the core into a shallow (.010 inch - .020 inch) suspension of -400 mesh powder suspended in clear nitrocellulose lacquer. After the suspension flowed to fillets and nodes by capillary action, the core was placed between glass or teflon plates and slowly rotated to maintain even distribution of the sink powder in the nodes until the lacquer dried.

If necessary, additional powder was placed at the fillets by re-dipping the edges of the core into a more viscous lacquer-powder suspension. Excess powder deposited along the edges of the core was then removed by a flat scraper. Close control of powder loading was achieved by this method. This process suggests manufacturing

TABLE IV

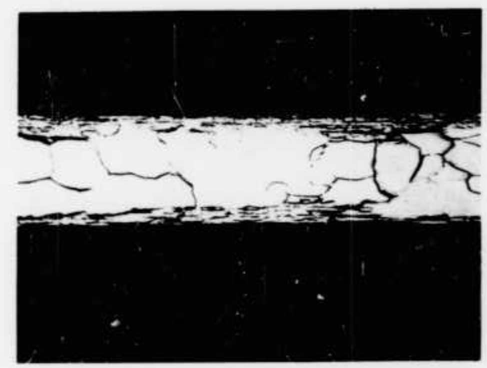
Ta-10W PRE-BRAZE CLEANING PROCEDURE

1. Vapor Degrease
2. Alkaline Clean - 6-10 oz/gal. Wyandotte WLC at 180F ± 10F for five to ten minutes or equivalent alkaline cleaner
3. Cold tap water rinse
4. Acid Etch

   25 Wt. % HF (40%)
   25 Wt. % HNO_3 (70%)
   50 Wt. % H_2O

   Use five minutes at room temperature for sheet and foil
5. Cold tap water rinse
6. Distilled water rinse
7. Alcohol dip (optional on sheet, preferable on core)
8. Air dry

Typical Weight Loss Data - 5-7% on .002 in. Ta-10W foil
2% on .010 in. Ta-10W sheet



NOTE SURFACE CONTAMINATION

MAG: 500X ETCHANT: MURAKAMI'S

RECRYSTALLIZED AT 2600F FOR 1 MIN. IN 300 MM ARGON

FIGURE 7 MICROSTRUCTURE OF RECRYSTALLIZED .002" TZM FOIL

TABLE V

TZM PRE-BRAZE CLEANING PROCEDURE

1. Vapor Oegrease

2. Alkaline Clean - 6-10 oz./gal. Wyandotte WLG at 180F ± 10F for five to ten minutes or equivalent alkaline cleaner

3. Cold tap water rinse

4. Alkaline Etch

   10 Wt. % NaOH
   5 Wt. % $KMnO_4$
   85 Wt. % H_2O
   Use five minutes at 90F ± 10F for facings
   Use fifteen minutes at 220F ± 10F for foil

5. Cold tap water rinse

6. Smut Removal

   15 cc. H_2SO_4 (96%)
   15 cc. HCL (38%)
   70 cc. H_2O
   12 gm. Chromic Acid
   Use five minutes at 120F ± 10F on facings
   Use ten minutes at 220F ± 10F for foil

7. Cold tap water rinse

8. Distilled water rinse

9. Alcohol dip (optional on facings, preferable on core)

10. Air dry

Typical Weight Loss Data - .5% on .013 in. TZM sheet
21% on .002 in. TZM foil

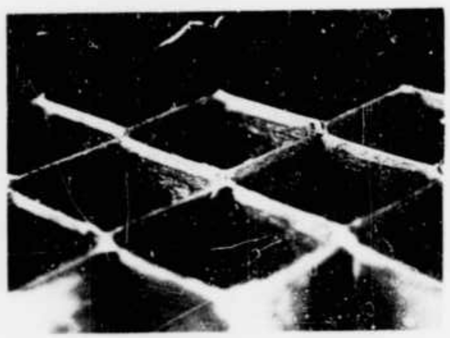
scale-up capability. Figure 8 shows a typical honeycomb specimen with diffusion sink powder placed at fillet and node areas.

Powder placement on tee joints is similar to that used for the honeycomb specimens. A typical brazed tee specimen consisting of a .002 inch foil and a .013 inch base sheet is shown in Figure 9.

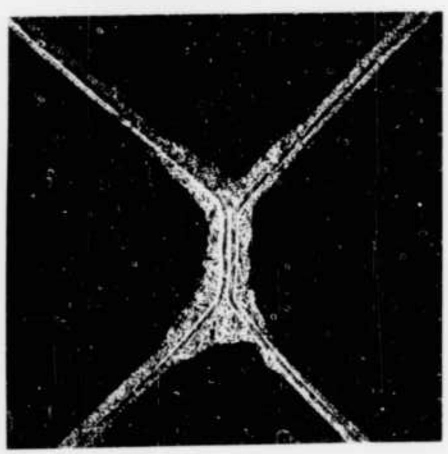
TZM Recrystallization Behavior

Recrystallization tests were conducted on the .002 inch and .013 inch TZM material to be employed in this program. These tests were conducted in vacuum using a heating rate of 600F/min. and a cooling rate of approximately 1500F/min. The results shown below will be employed to establish maximum thermal processing exposures.

Exposure	% Recrystallization .013 in. TZM sheet Lot 7312	% Recrystallization .002 in. TZM foil Heat KDTZM 9364
2475F, 1 min.		25
2520F, 1 min.		50
2550F, 2 min.	10	
2600F, 1 min		100
2675F, 1 min.	30	
2750F, 1 min.	100	



FILLET AND NODE AREAS
MAGNIFICATION 5X



NODE AREA
MAGNIFICATION 25X

FIGURE 8 HONEYCOMB SPECIMEN WITH DIFFUSION SINK POWDER PLACED AT FILLETS AND NODES

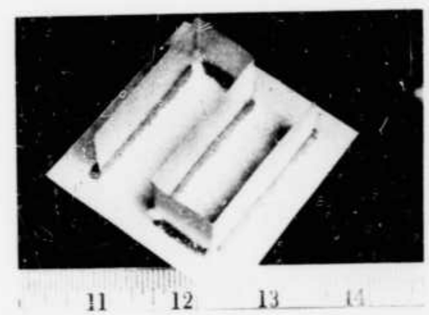


FIGURE 9 TYPICAL .002" - .013" BRAZED TEE JOINT SPECIMEN

III CONCLUSIONS

1. A literature survey indicated that no completely satisfactory brazing systems have been developed for brazing molybdenum and tantalum alloys.

2. The diffusion sink and reactive brazing concepts show the most promise for increasing braze joint remelt temperatures.

3. In general, titanium-base alloys show the most promise for diffusion sink brazing molybdenum and tantalum alloys.

4. In general, columbium-base alloys show the greatest potential for conventional brazing of tantalum alloys.

5. A number of braze systems have been selected for evaluation on the TZM and Ta-10W alloys.

6. A potential oxidation protection coating/braze alloy compatibility problem exists for both TZM and Ta base alloys using conventional coating systems.

7. Cleaning procedures have been selected for pre-braze cleaning of TZM and Ta-10W.

8. Techniques have been developed for placing diffusion sink powders at the fillet and node areas of honeycomb specimens.

IV FUTURE WORK

The following effort is scheduled for the next quarter.

1. Complete the selection of braze alloys for tee joint evaluation.

2. Complete powdering of braze alloys.

3. Initiate evaluation of braze systems on tee joints, lap joints, and small honeycomb specimens.

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